

THERMAL EXPANSION OF SOME ALKALI FLUORIDES AND MAGNESIUM OXIDE BY X-RAY DIFFRACTION

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ABSTRACT In this paper high temperature X-ray data on the thermal expansion of LiF, NaF and MgO are reported for the first time. The results are compared with the macroscopic observations wherever available. The role of lattice defects is examined and the applicability of Debye-Grimmson equation to explain the observed variation of thermal expansion with temperature is discussed.

INTRODUCTION

The coefficient of thermal expansion α of almost all ionic crystals increases with temperature. Lawson (1950) assumed that α should be constant for a perfect crystal lattice and deduced that in such a crystal defects do play a part and contribute to the thermal expansion. He succeeded in proving his point in the case of silver bromide but not for silver chloride. It was pointed out in our previous communication (Pathak and Pandya, 1960 (b)) that in the case of ionic crystals Schottky defects shall predominate and that if defects did contribute to the thermal expansion of a crystal, the value of α determined by macroscopic methods should be greater than that measured by the X-ray method. On searching the literature it was found that the high temperature X-ray data for the salts examined in the present experiments were not available.

Lithium fluoride has been studied by Adenstedt (1936) in the low temperature region upto about -225°C . It has also been studied by Eucken and Dannöhl (1934) by the heterodyne beat method and by Sharma (1950) by an interferometric method.

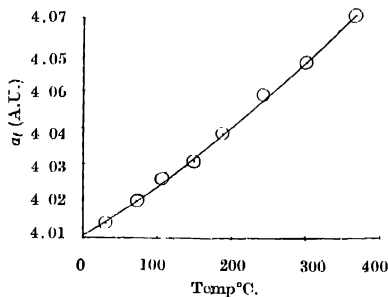
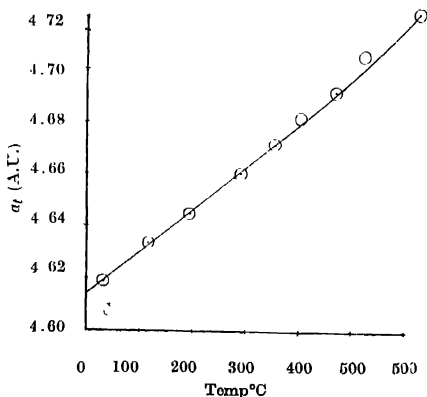
Sodium fluoride has been investigated at low temperatures by Henglein (1925) by the pycnometer method. Room temperature values are quoted by Megaw (1939) and Wooster (1949). It has been recently investigated upto 254°C by Deshpande (1961)

The thermal expansion of magnesium oxide was studied by Fizeau (1867), Goodwin and Mailey (1909) from 120°C to 270°C and Merrit (1926). It has been systematically examined by optical or interferometric methods by Thilonius and Holzmann (1930) upto 1200°C , Austin (1931) upto 800°C , Durand (1936) upto 85°C and Sharma (1950) upto about 700°C . No systematic high temperature X-ray data on this salt are available in the literature.

The observations in the present work were taken by employing a diffractometer, Geiger counter and a ratemeter. The diffractometer had a diameter of 500 mm. and was calibrated in degrees (2θ , each degree divided into four parts). The position of the Geiger counter could be read upto one minute of arc and by estimation upto $\frac{1}{2}$ minute. The error in the measurement of the cell constant a_c is estimated to be less than ± 0.002 .

OBSERVATIONS AND RESULTS

The same small furnace (Pathak and Pandya, 1959) was used in this work which was employed in the earlier measurements on NaCl (Pathak and Pandya, 1959), CsI (Pathak and Pandya, 1960a) and KBr, KI and CsBr (Pathak and Pandya, 1960b). The results of the present measurements are shown in Figs. 1, 2, 3 and Table I.

Fig. 1. LaF_3 .Fig. 2. NaF .

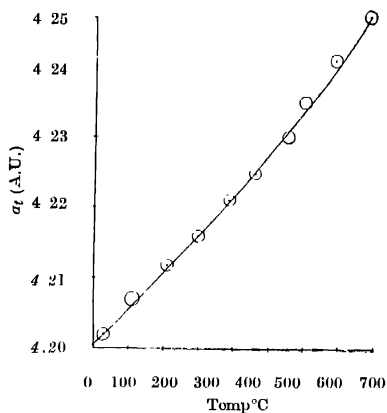


Fig. 3. MgO.

The equations satisfying the smooth curves drawn from the observed points are given below :

$$\text{LiF} \cdot \quad a_t = 4.0102 + 1.312 \times 10^{-4}t + 9.160 \times 10^{-8}t^2$$

$$\text{NaF} \cdot \quad a_t = 4.614 + 1.452 \times 10^{-4}t + 5.595 \times 10^{-8}t^2$$

$$\text{MgO} \cdot \quad a_t = 4.2015 + 4.625 \times 10^{-5}t + 1.392 \times 10^{-8}t^2$$

The coefficient of expansion α was calculated from the equation $\alpha = \frac{1}{a_t} \cdot \frac{da_t}{dt}$.

The comparison of our results with those of others is shown in Tables II, III and IV.

TABLE I

LiF		NaF		MgO	
Temperature degree C	$\alpha \times 10^6$	Temperature degree C	$\alpha \times 10^6$	Temperature degree C	$\alpha \times 10^6$
30	34.1	30	32.2	27	11.2
72	35.9	72	33.1	208	12.3
150	39.4	116	34.2	386	13.5
187	41.0	195	35.9	552	14.6
242	43.3	288	38.1	691	15.4
301	45.9	351	39.5	788	16.0
367	48.7	400	40.6		
		467	42.1		
		520	43.2		
		625	45.5		

TABLE II
Lithium fluoride

Temperature degree C	$\alpha \times 10^6$		
	Authors	Sharma	Eucken and Dannöhl
0	32.7	33.8	32.2
30	34.1	34.4	33.4
72	35.9	35.5	35.2
150	39.4	37.9	38.4
187	41.0	38.9	40.0
242	43.3	41.6	42.2
301	45.9	44.4	44.6
367	48.7	47.8	47.4

TABLE III
Sodium fluoride

Temperature degree C	$\alpha \times 10^6$	
	Deshpande	Authors
30	34.0	32.2
72	35.2	33.1
116	36.5	34.2
195	38.8	35.9
288	41.5	38.1

DISCUSSION OF THE RESULTS

X-ray data on LiF at high temperatures are not available and hence it is not possible to compare our results with those of other workers. In Table II, however, comparison with the macroscopic data of Sharma (1950) and those of Eucken and Dannöhl (1934) is shown and it is seen that the agreement is fairly good.

Our results on NaF are compared with the X-ray data of Deshpande (1961) in Table III. Our results are slightly lower. Our α at 0°C viz. 31.5×10^{-6} may also be compared with that of Henglein between -79°C and 0°C viz. 33.0×10^{-6} .

Comparison of our X-ray data on MgO with the macroscopic observations of other workers is shown in Table IV. Our results agree excellently well with those of Sharma (1950). They also agree fairly well with those of Thilenius and Holzmann (1930). Austin's (1931) results are too erratic in the low temperature region with our results at high temperatures.

TABLE IV
Magnesium oxide

Temperature degree	$\alpha \times 10^6$		
	Literature	Sharnau	Authors
40	10.4 ¹	11.2	11.3
120-270	12.1 ²	12.2	12.3
25-800	13.4 ³	13.7	13.6
63.7	11.2 ¹	11.4	11.4
153	11.9 ⁴	11.9	12.0
246.3	12.8 ⁴	12.5	12.6
348.2	13.8 ⁴	13.1	13.2
448.4	14.1 ⁴	13.8	13.9
546.1	14.6 ⁴	14.5	14.5
645.8	12.2 ⁴	15.2	15.2
745.5	15.7 ⁴	16.0	15.8
20-55	6.7 ⁵	11.2	11.3
20-100	9.1 ⁵	11.3	11.4
20-150	10.4 ⁵	11.5	11.6
20-200	10.9 ⁵	11.6	11.7
20-300	11.6 ⁵	12.0	12.0
20-400	12.1 ⁵	12.3	12.4
20-600	13.0 ⁵	13.0	13.0
20-800	13.5 ⁵	13.7	13.5

1 Fizeau (1867)

2 Goodwin and Mailey (1909)

3 Merritt (1926)

4 Thilonius and Holzmam (1930)

5 Austin (1931)

It can be seen from the above discussion that comparison with macroscopic results are possible only in the case of lithium fluoride and magnesium oxide. In the case of the former the X-ray expansions are greater than the macroscopic ones. If lattice defects played any part the reverse should have happened. In

TABLE V
Grüneisen parameters

Substance	$Q/2R \times 10^3$	$3p$	References
Lithium	29.01	12.01	Present values
fluoride	29.4	11.5	Eucken and Dannohl
	26.2	—	Equation (2)
Sodium	29.54	8.0	Present values
fluoride	29.25	—	Equation (2)
Magnesium	61.15	15.10	Present values
oxide	61.76	—	Equation (2)

the case of magnesium oxide the X-ray data and the macroscopic data agree perfectly. The defects, if any, therefore, affect the X-ray and the macroscopic expansions equally or their contribution to the thermal expansion is negligible.

It can be shown (Pathak and Pandya, 1960b) from the Debye-Grüneisen theory that

$$\frac{a_0}{a_T - a_0} = \frac{Q}{2R} \cdot \frac{1}{TD(\theta/T)} - 3p \quad \dots (1)$$

Where a_0 and a_T are the cell constants at 0°K. and T°K. respectively, $D(\theta/T)$ the Debye function and $Q/2R$ and $3p$ are constants called the Grüneisen's parameters. The above equation shows that for a crystal obeying Grüneisen's law the graph of $a_0/a_T - a_0$ against $1/TD(\theta/T)$ should be a straight line. In the case of substances examined in the present experiments such graphs are found to be straight lines. The Grüneisen's parameters determined from these graphs are compiled in Table V. The value of Q can also be determined from the relation

$$Q = V_0/\gamma K_0 \quad \dots (2)$$

where K_0 and V_0 are the compressibility and molar volume at 0°K. The values of $Q/2R$ calculated from this equation are also given in Table V for comparison, the values of V_0 and γ being taken from Born and Huang (1954).

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